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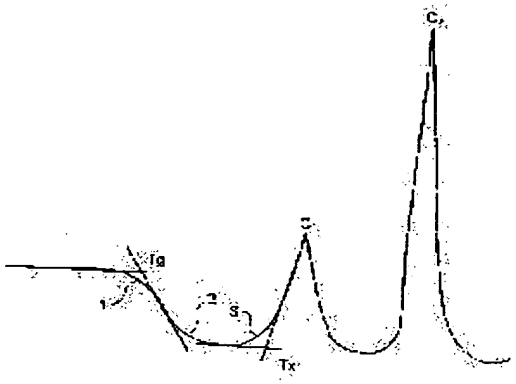
(54) BIOLOGICALLY ACTIVE CRYSTALLIZED GLASS BEADS

(57)Abstract:
PROBLEM TO BE SOLVED: To obtain the subject glass beads capable of giving biologically active cement having high mechanical strength and slight in its decline and suitable as a biologically active filler for biologically active cement.
SOLUTION: The biologically active glass beads are obtained by crystallizing such glass beads as to contain Ca and be <120° C in the difference between the glass transition point (Tg) determined by DTA and the temperature (Tx1) at which the 1st crystal begins to deposit.



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CLAIMS

[Claim(s)]
[Claim 1] The living body activity crystallization glass bead characterized by making it come to crystalize the glass bead which has the property in which the difference of the temperature (Tx1) to which calcium is contained and the glass transition point (Tg) in DTA (differential thermal analysis) and the 1st crystal begin to deposit is less than 120 degrees C.
[Claim 2] It is CaO at mass %. 30 - 70%, SiO2 30 - 70%, P2O5 0 - 40%, MgO 0 - 20%, CaF2 Living body activity crystallization glass bead of claim 1 characterized by having 0 - 5% of presentation.

[Claim 3] Claim 1 or 2 living body activity crystallization glass beads which are characterized by the crystal of wollastonite and/or a JIOPU side depositing on the front face.
[Claim 4] The living body activity crystallization glass bead of claims 1-3 characterized by the crystal of an apatite depositing.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention relates to the living body activity crystallization glass bead used as the filler of living body activity cement, or a bulking agent of the bone deficit section.
[0002]
[Description of the Prior Art] PMMA cement is widely known as cement used for adhesion immobilization of the implant material used in the orthopedics field, the oral surgery field, etc., restoration of the bone deficit section, reconstruction of the cranial deficit section in the neurosurgery field, etc. However, since there is no living body activity in PMMA cement, it is uncombinable with a natural bone and a chemistry target. Then, the living body activity cement which added living body activity ingredients, such as calcium content glass, as a filler with PMMA cement is proposed in recent years.
[0003]
[Problem(s) to be Solved by the Invention] Top Norio object activity cement is combinable with a natural bone and a chemistry target, as a result of eluting calcium2+ ion from the living body activity filler exposed to the hardening body surface, reacting with body fluid and forming an apatite layer in a hardening body surface, if it hardens in the living body.
[0004] However, if this cement has a low mechanical strength and is embedding cement inside of the body for a long period of time, a mechanical strength will tend to deteriorate by pervasion by body fluid.
[0005] The purpose of this invention has a high mechanical strength, and it is degradation of a mechanical strength being able to produce little living body activity cement, and offering a living body activity crystallization glass bead suitable as a living body activity filler of living body activity cement moreover.
[0006]
[Means for Solving the Problem] The living body activity crystallization glass bead of this invention contains calcium, and is characterized by making it come to crystalize the glass bead which has the property in which the difference of the temperature (Tx1) to which the glass transition point (Tg) in DTA and the 1st crystal begin to deposit is less than 120 degrees C.
[0007]
[Embodiment of the Invention] The property of living body activity cement, especially a mechanical strength are sharply influenced by the class of living body activity filler, the configuration, etc. Since the living body activity crystallization glass beads of this invention are glass ceramics, a mechanical strength is high and there is also little pervasion by body fluid compared with glass, the engine performance of living body activity cement cannot deteriorate easily. And since this living body activity crystallization glass bead contains calcium, it has living body activity.
[0008] Moreover, the crystallization glass bead of this invention is produced using the glass bead which has the property in which the difference of the temperature (Tx1) to which the glass transition point (Tg) in DTA and the 1st crystal begin to deposit is less than 120 degrees C: This glass bead is crystallized with the original form stopped without the front face of a glass particle

melting and particles welding, in order that a crystal may deposit at an early stage and may control a softening flow of glass, if it heat-treats. The crystallization glass bead of this invention has the spherical gestalt almost equivalent to the glass bead before crystallization because of this. When this is used as a filler of cement, since a spherical gestalt can prevent the stress concentration generated in cement, it can raise a mechanical strength further. On the other hand, if the difference of Tx1 and Tg becomes 120 degrees C or more, before a crystal deposits, a softening flow will occur, particles will adhere, and spherical glass ceramics will not be obtained. And a grinding process is needed for using it as a filler.

[0009] If wollastonite and a JIOPU side are deposited as a class of crystal, the film will be stretched by the front face of a particle and the effectiveness of preventing joining of particles will become still higher. If the case where they are the case where a crystal is wollastonite, and a JIOPU side is compared, since wollastonite has much elution of ion, high living body activity will be acquired. On the other hand, since the mechanical strength of the very thing is high, as for a JIOPU side, chemistry endurance becomes high still more highly [reinforcement]. With the property to need, the crystal of wollastonite and/or a JIOPU side can be deposited and a materials design can be carried out.

[0010] It is desirable that the apatite deposits, in order to raise biocompatibility to a living body activity crystallization glass bead.

[0011] The presentation range of the living body activity crystallization glass bead of this invention is CaO at mass %. 30 - 70%, SiO2 30 - 70%, P2O5 0 - 40%, MgO 0 - 20%, CaF2 It is 0 - 5%, and these glass ceramics show living body activity, and if a mechanical strength is high and moreover uses it as a filler for cement, they can raise the mechanical strength of a cement hardening object remarkably. It is CaO at mass % especially preferably. 38 - 54%, SiO2 32 - 50%, P2O5 7 - 25%, MgO 0.5 - 16%, CaF2 It has 0 - 2% of presentation. It is easy to crystallize the glass of this presentation, with a globular form maintained.

[0012] When using the living body activity crystallization glass bead of this invention as a filler for cement, it is desirable to carry out silane coupling processing of the front face. While familiarity by the resinous principle becomes good and the reinforcement of a cement hardening object becomes large by this processing, since a powder front face has a hydrophobic group, the inhibition nature of blood is lost, and it becomes easy to harden cement. In addition, in performing silane coupling processing, it is desirable to carry out in weak acid - a neutral region (about five to eight pH). This is because a glass front face will corrode, living body activity will become low, if pH is lower than 5, and silane coupling processing will become difficult if pH is higher than 8.

[0013]

[Example] Hereafter, this invention is explained to a detail based on an example and the example of a comparison.

[0014]

[Table 1]

	実施例					比較例	
	1	2	3	4	5	6	7
組成（質量%）							
CaO	41	43	44	43	40	55	60
SiO_2	40	35	40	41	37	27	28
P_2O_5	15	16	14	15	13	15	18
MgO	4	6	2	1	10	3	4
DTA（℃）							
Tx	800	790	840	815	850	825	860
Tg	720	720	740	730	750	700	730
ΔT	80	70	100	85	100	125	130
粒子の溶着	無し	無し	無し	無し	無し	有り	有り
生体活性の有無	有り	有り	有り	有り	有り	有り	有り
表面析出結晶*)	Wol	Wol	Wol	Wol		Wol	Wol
（X線回折）	Dio	Dio	Dio		Dio	Dio	

*) Wol：Wollastonite（$CaO \cdot SiO_2$）
Dio：Diopside（$CaO \cdot MgO \cdot 2SiO_2$）

[0015] Table 1 shows the example (sample No.1-5) and the example of a comparison (6 No. 7) of a living body activity crystallization glass bead of this invention.
[0016] Each sample was prepared as follows. First, the glass bead was obtained by spraying it for glass into a gas burner flame 1500 degrees C or more, after grinding, melting and so that it may become the presentation of Table 1. The crystallization glass bead was obtained by heat-treating the obtained glass bead at 900 degrees C.
[0017] It evaluated [sample / which was produced in the above procedures / each] about the existence of DTA, the joining nature of a particle, and living body activity, and a deposit crystal. The result is shown in Table 1.
[0018] In addition, the sample of DTA measured Tg and Tx1 by the Rigaku thermal-analysis device ThermoflexDTA8121 using what ground with the mortar the glass bead obtained as mentioned above. With the speed of 10 degrees C / min, the temperature up of the Measuring condition was carried out, and it was measured to 1000 degrees C. The DTA curve was shown in drawing 1 . As shown in drawing 1 , the 1st point of inflection 1 of after measurement initiation appears, and endoergic [accompanying the abrupt change of the glass in a glass transition field] arises. Next, the 2nd point of inflection 2 appears and an endoergic condition becomes fixed. The 3rd point of inflection 3 where a crystal begins to deposit appears after this, and then the exothermic peaks C1 and C2 by crystal deposit appear. Tg (transition point of glass) can be calculated by the intersection of the tangent which meets a baseline, and the tangent in alignment with the curve from the 1st point of inflection 1 to the 2nd point of inflection 2. Tx1 (temperature to which a crystal begins to deposit) can be calculated by the intersection of the tangent in alignment with the curve from the 2nd point of inflection 2 to the 3rd point of inflection 3, and the tangent in alignment with the curve from the 3rd point of inflection 3 to an exothermic peak C1. Respectively, for the magnetic pan, it was made to crystallize at 900 degrees C, and the deposit crystal identified the glass bead with the Rigaku X-ray diffractometer. Whether there is any joining of particles checked the particle after crystallization with viewing and an optical microscope. the existence of living body activity -- apatite ****** -- whether an apatite deposits in the so-called false body fluid estimated. Specifically, apatite organization potency observed and evaluated after immersion whether the needle crystal of an apatite would deposit by the electron microscope on the particle front face for three days to 37-degree C false body fluid.
[0019] In order that the difference of Tg and Tx1 might produce the sample of No.1-5 which are an example using the glass bead which is less than 120 degrees C in DTA so that clearly from Table 1, particles did not weld these all at the time of crystallization, but, moreover, the spherical thing was checked. on the other hand, No. which is an example of a comparison -- in order that

the difference of Tg and Tx1 in DTA may produce the sample of 6 and 7 using the glass bead which is 120 degrees C or more -- this -- both, at the time of crystallization, the mutual particle carried out joining unification and did not become spherical. Moreover, it was checked that an apatite deposits on a sample front face in false body fluid, and an example and the example of a comparison have living body activity, the crystal of wollastonite and/or a JIOPU side deposited in the particle front face after crystallization, and, as for the interior, the apatite deposited as a main crystal.

[0020]

[Table 2]

	実施例			比較例
	A	B	C	D
フィラー(表1)	1	3	5	1
セメント曲げ強度 (MPa)				
初期強度	130	135	135	100
6カ月後	120	120	130	80

[0021] Table 2 shows the example (sample A-C) which used the crystallization glass bead of this invention as a living body activity filler of cement, and the example of a comparison (sample D) using the glass bead as a living body activity filler of cement.

[0022] Living body activity cement was adjusted as follows.

[0023] A living body activity filler and polymethacrylate powder were prepared first.

[0024] As a living body activity filler, No.1 of Table 1 and the crystallization glass bead of 3 and 5 were used for sample A-C, and the glass bead before crystallization of No.1 was used for Sample D. In addition, these beads performed surface treatment using the silane coupling agent adjusted to pH6.

[0025] As polymethacrylate system powder, 4 micrometers of mean diameters and the polymethylmethacrylate (PMMA) powder of a mean molecular weight 200,000 were prepared.

[0026] Next, weighing capacity of the polymethacrylate system powder was carried out to the living body activity filler by the weight ratio of 50:50, and the benzoyl peroxide was further added as a polymerization initiator, and it mixed.

[0027] Moreover, methyl methacrylate (MMA) was prepared as a methacrylate system monomer, and N and N-dimethyl-para toluidine was further added and kneaded as a polymerization promotor.

[0028] Thus, the cement sample of a powder-liquid system was obtained.

[0029] In addition, the addition of benzoyl-peroxide, N, and N-dimethyl-para toluidine was made into 2 weight sections and the 1.4 weight section to the total amount 100 weight section of a monomer, respectively so that it might harden in about 7 minutes.

[0030] Thus, the produced cement was stiffened and flexural strength was evaluated. The result is shown in Table 2. In addition, flexural strength produced the test piece with a magnitude of 3x4x20mm, and to false body fluid, one day (first stage) and after being immersed for six months, it evaluated them by the three-point bending test.

[0031] Although the mechanical strength which most flexural strength of the cement which used the crystallization glass bead of this invention maintained early reinforcement, and was excellent is shown so that clearly from Table 2, it is thought that degradation on the strength from the first stage of the flexural strength of the cement which used the glass bead is large, and it has a problem to real use on the other hand.

[0032]

[Effect of the Invention] As explained above, its mechanical strength is high, and since the crystallization glass bead which has the living body activity of this invention does not almost have degradation of a mechanical strength, the use as a bulking agent of the living body activity filler of cement or the bone deficit section is possible for it.

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]
[Drawing 1] It is drawing showing the typical differential-thermal-analysis (DTA) curve of the example glass of this invention.
[Description of Notations]
1 .... The 1st point of inflection
2 .... The 2nd point of inflection
3 .... The 3rd point of inflection
Tg ... The transition point of glass
Tx1 .. Temperature to which the first crystal begins to deposit
C1 ... First crystallization peak temperature
C2 ... Second crystallization peak temperature

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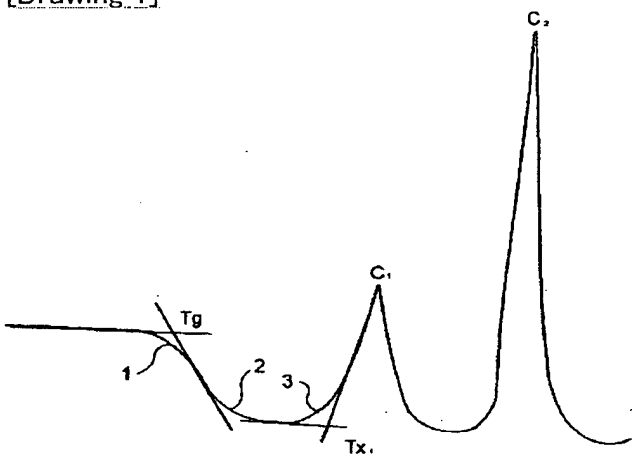
DRAWINGS

[Drawing 1]



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